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COLLABORATIVE STUDY OF METHOD FOR THE DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES (FOSSIL FUEL-FIRED STEAM GENERATORS)

Henry F. Hamil, et al

Southwest Research Institute

Prepared for:

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16. ABSTRACT This report presents the results obtained from a collaborative test of Method 5, a test procedure for determining particulate emissions from stationary sources. Method 5 specifies that particulate matter be withdrawn isokinetically from the source and its weight determined gravimetrically after the removal of uncombined water. The test was conducted at a fossil fuel-fired steam generating power plant using four collaborative laboratories. Sixteen sample runs were made over a two-week period by the collaborators for a total of 63 individual determinations. The reported values of one of the laboratories were not included in the analysis. Conversation with other personnel who participated in the test, and inspection of the laboratory's sampling train subsequent to the test, provided information which indicated that the determinations made were not representative of Method 5 results. Of the remaining determinations, one was eliminated due to failure to maintain isokinetic conditions. The remaining values were subjected to statistical analysis to estimate the precision that can be expected with field usage of Method 5. The precision estimates are expressed as standard deviations, which are shown to be proportional to the mean determination, δ, and are summarized as follows: (a) Within-lab: The estimated within-lab standard deviation is 31.1% of δ, with 34 degrees of freedom; (b) The estimated between-lab standard deviation is 36.7% of δ, with 2 degrees of freedom; (c) From the above, we can estimate a laboratory bias standard deviation of 19.5% of δ.

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by
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SwRI Project No. 01-3487-01
EPA Contract No. 68-02-0623

Prepared for

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June 30, 1974

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SUMMARY AND CONCLUSIONS

This report presents the results obtained from a collaborative test of Method 5, a test procedure for determining particulate emissions from stationary sources. Method 5 specifies that particulate matter be withdrawn isokinetically from the source and its weight determined gravimetrically after the removal of uncombined water.

The test was conducted at a fossil fuel-fired steam generating power plant using four collaborating laboratories. Sixteen sample runs were made over a two-week period by the collaborators for a total of 63 individual determinations.

The reported values of one of the laboratories were not included in the analysis. Conversation with other personnel who participated in the test, and inspection of the laboratory's sampling train subsequent to the test, provided infomation which indicated that the determinations made were not representative of Method 5 results.

Of the remaining determinations, one was eliminated due to failure to maintain isokinetic conditions. The remaining values were subjected to statistical analysis to estimate the precision that can be expected with field usage of Method 5. The precision estimates are expressed as standard deviations, which are shown to be proportional to the mean determination, δ, and are summarized below.

(a) Within-laboratory: The estimated within laboratory standard deviation is 31.1% of δ, with 34 degrees of freedom.

(b) The estimated between-laboratory standard deviation is 36.7% of δ, with 2 degrees of freedom.

(c) From the above, we can estimate a laboratory bias standard deviation of 19.5% of δ.

The above precision estimates reflect not only operator variability, but, to an extent, source variability which cannot be separated from these terms. The results summarized above were obtained from a single test using the data from three collaborators. Further testing would, of course, be necessary to obtain conclusive results.

Comments on the use of Method 5 from the collaborators are included, and recommendations are made for the improvement of the method.

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I. INTRODUCTION

This report describes the work performed and results obtained on Southwest Research Institute Project 01-3487-001, Contract No. 68-02-0623, which includes collaborative testing of Method 5 for particulate emissions as given in "Standards of Performance for New Stationary Sources."[1]*

This report describes the collaborative testing of Method 5 in a coal-fired steam generating power plant and gives the statistical analysis of the data from the collaborative tests, and the conclusions and recommendations based on the analysis of data.

*Superscript numbers in parentheses refer to the List of References at the end of this report.

II. COLLABORATIVE TESTING OF METHOD 5

A. Collaborative Test Site

Arrangements were made for collaborative testing of Method 5 at the Allen King Power Plant of Northern States Power Company near St. Paul, Minnesota. Through a subcontract with Thermo-Systems, Inc., access to the plant, sampling ports and platforms, and other sampling facilities were provided, and logistical support obtained. Facilities were installed which provide for simultaneous sampling by four collaborators, each collaborating team working on a separate platform with a separate sampling port.

The power plant was visited in December, 1972 to inspect the facilities being constructed and to investigate several potential problems including length of probe required, effect of positive pressure in the duct, and statistical details of planning and conducting collaborative tests.

Table 1 gives some information on the Allen King Power Plant, and Figure 1 shows a view of the power plant. Figure 2 shows the overall site configuration, and the sample site configuration is in Figure 3. Velocity profiles across the sampling area within the duct are shown in Figure 4. The profiles were obtained by averaging the velocities of all four collaborators at each traverse point from four randomly selected sampling runs. Due to the width of the duct, a wall-to-wall traverse could not be made with a 10-foot probe. Sampling the entire duct width would have required sampling from the center line of the duct out to the wall on all four ports for a single sampling run. This procedure would have required moving all four sampling trains through a 34-inch high crawl way underneath the duct on each run, and due to the time required would have precluded taking two samples per day. Since this study involved evaluation of

TABLE 1. GENERAL INFORMATION–ALLEN KING POWER PLANT

Rated Capacity–550 megawatts
(Normally Operated nearly full load at all times)

Age of facility	5 yr
Stack height	800 ft
Stack diameter	26 ft at bottom, 18 ft at top
Coal usage at full load	240 tons/hr
Coal used	Southern Illinois
Coal sulfur content	3-1/4 percent

A small amount of Montana coal (sulfur content about 1-1/2 percent) is available for use during pollution alerts. Combustion chamber consists of twelve cyclone units exhausting into a common heat exchanger system. The emission gas splits into two identical gas streams shortly upstream of twin electrostatic precipitators which normally collect 98 to 99 percent of the fly ash (by weight). The twin emission gas streams meet again at the base of the vertical stack. Our sampling ports for the collaborative tests are in the south–left horizontal duct, just upstream of the vertical stack. Approximately 1 million cfm of emission gas passes through each of the twin emission gas streams.

Internal horizontal duct dimensions at sampling ports	27 ft high 12 ft wide

Two sampling ports, one on each side of the duct, are located 6 ft above the center line of the duct; and two sampling ports, one on each side of the duct, are located 6 ft below the center line of the duct. The opposing ports are offset 6 in. vertically to prevent interference.

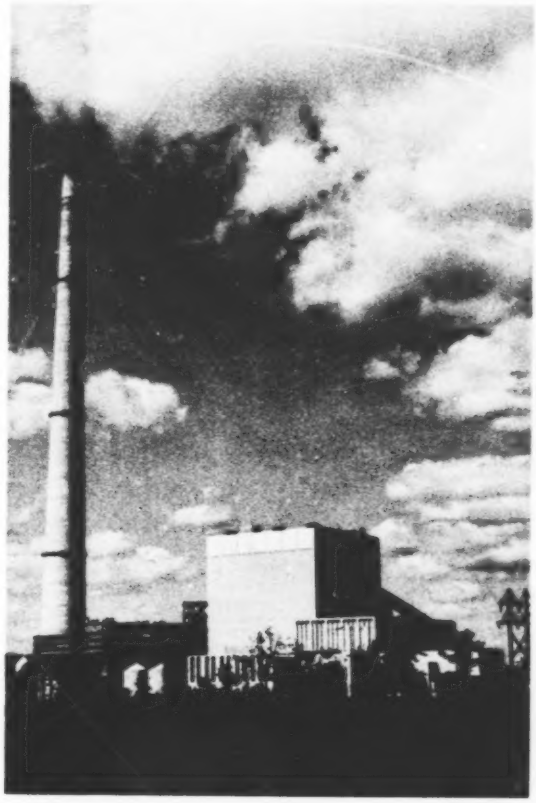


FIGURE 1. ALLEN KING POWER PLANT
NORTHERN STATES POWER AND LIGHT CO.

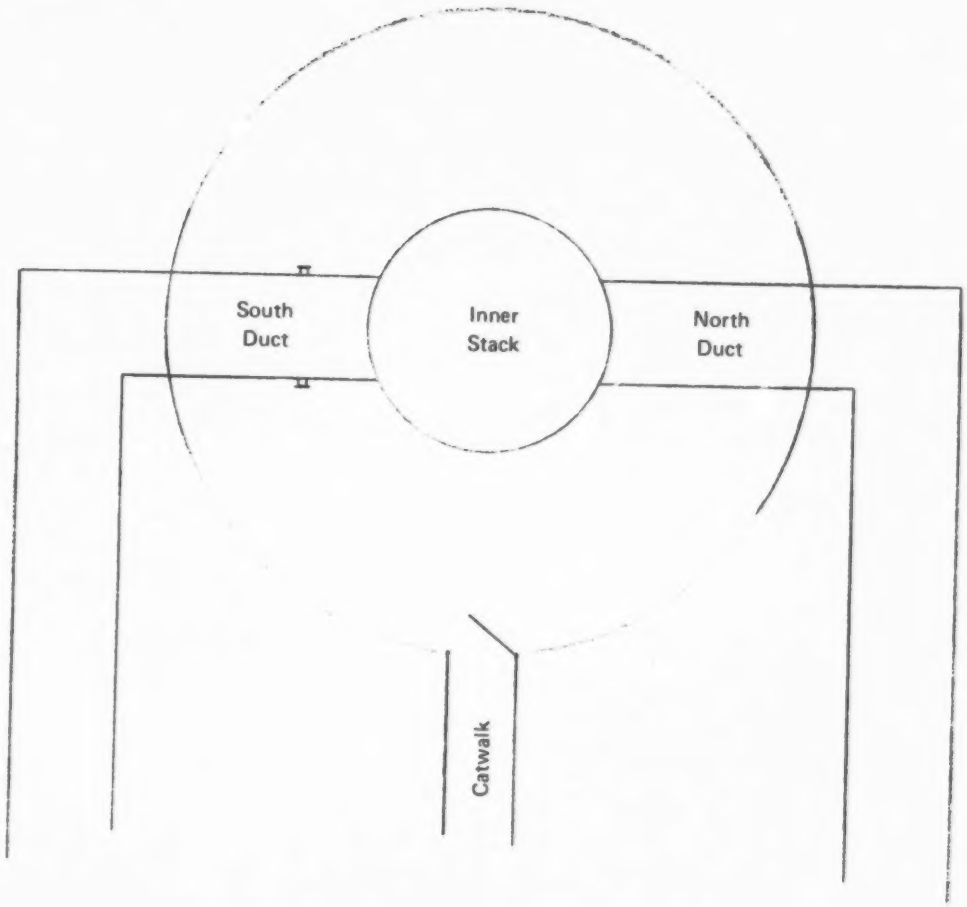
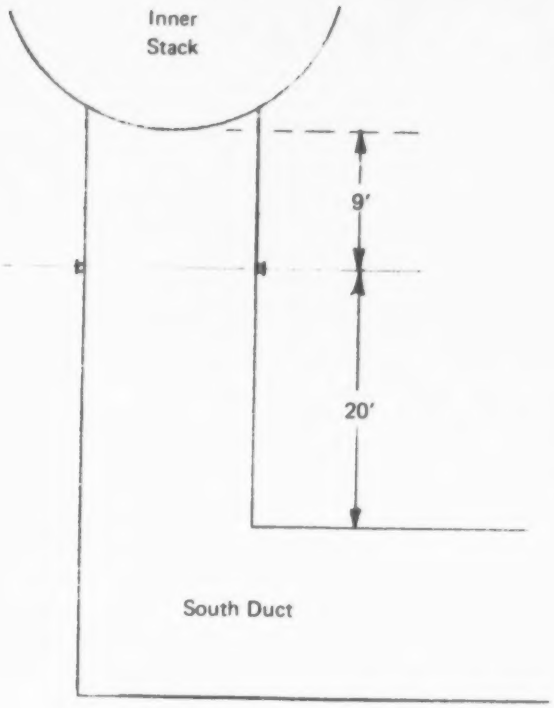


**FIGURE 2 ALLEN KING POWER PLANT
OVERALL SITE CONFIGURATION**



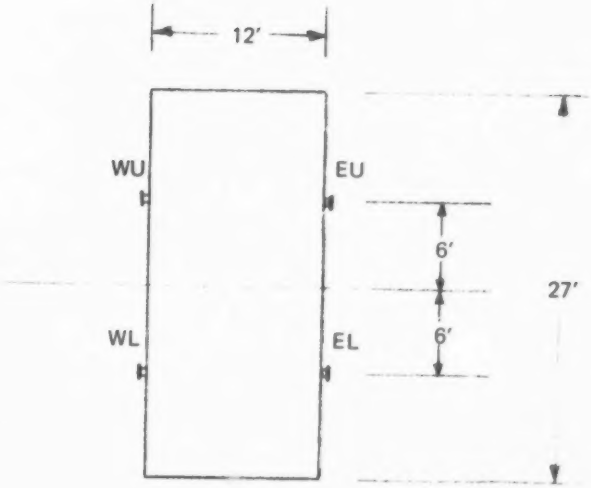
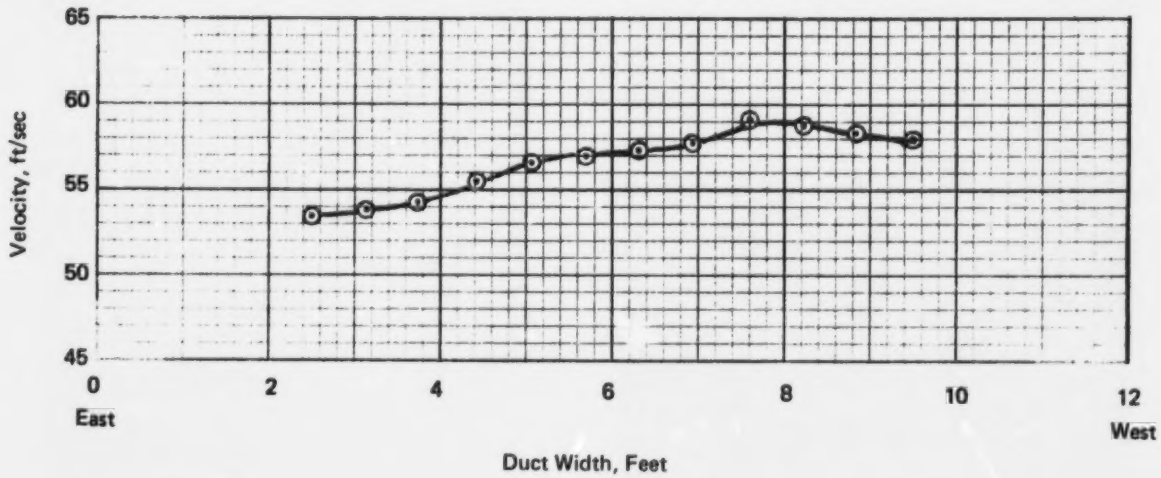
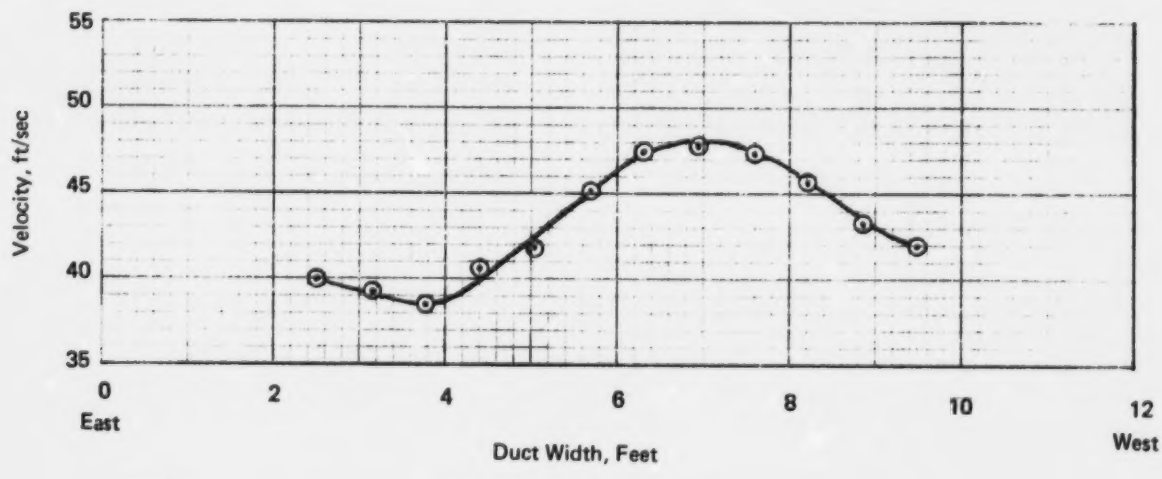


FIGURE 3. ALLEN KING POWER PLANT
SAMPLING SITE CONFIGURATION



Profile Across Upper Ports



Profile Across Lower Ports

FIGURE 4. AVERAGE VELOCITY PROFILES

Method 5 rather than characterization of the site, a modified tranversing procedure was adopted in which the samples were obtained from a seven-foot wide section of the duct, beginning and ending two and one-half feet from the interior duct walls. This seven-foot section could be traversed from either side of the duct, so that a sampling run consisted of taking one-half the sample from an upper (or lower) port, followed by a port change, and taking the other half of the sample from the other port on the same side of the duct. A total of 24 traverse points, 12 on each port, were used on each run. Figure 5 shows an overall view of the sampling platforms and ports on one side of the duct, while Figure 6 shows a view of an individual work area and sample port.

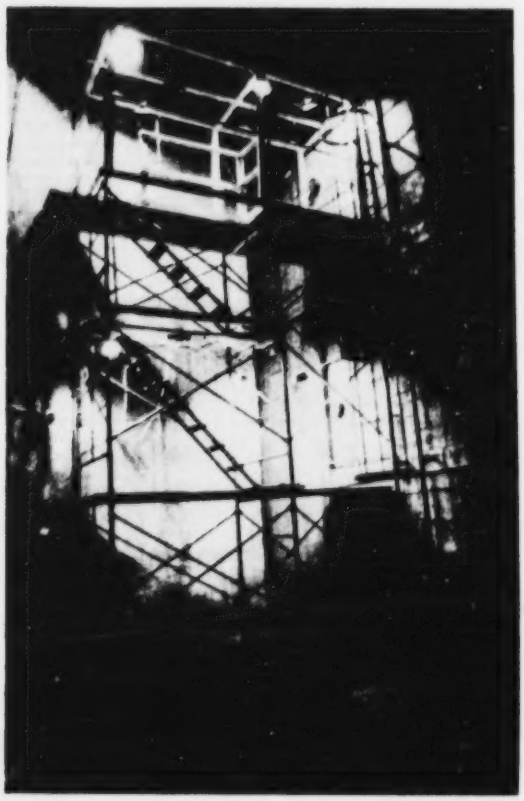


FIGURE 5. SAMPLE PLATFORMS AND PORTS

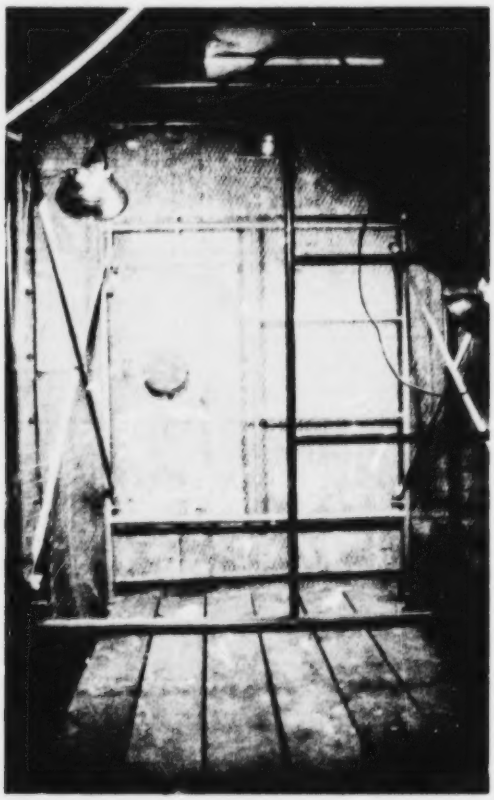


FIGURE 6. WORK AREA AND SAMPLE PORT

B. Collaborators

The collaborators for the Allen King Power Plant test were Mr. Mike Taylor and Mr. Hubert Thompson of Southwest Research Institute, Houston Laboratory, Houston, Texas; Mr. Charles Rodriguez and Mr. Ron Hawkins of Southwest Research Institute, San Antonio Laboratory, San Antonio, Texas; Mr. Gilmore Sem, Mr. Vern Goetsch, and Mr. Jerry Brazelli of Thermo-Systems, Inc, St. Paul, Minn.; and Mr. Roger Johnson and Mr. Harry Patel of Environmental Research Corporation, St. Paul, Minn.* As mentioned earlier in the report, Thermo-Systems, Inc. had the responsibility for site preparation and liaison between test crews and plant personnel.

Collaborative tests were conducted under the general supervision of Mr. Nollie Swynnerton of Southwest Research Institute. Mr. Swynnerton had the overall responsibility for assuring that the test was conducted in accordance with the collaborative test plan and that all collaborators adhered to Method 5 as written in the *Federal Register*, December 23, 1971. The collaborating teams for the test were selected by Dr. Henry Hamil of Southwest Research Institute.

*Throughout the remainder of this report, the collaborative laboratories are referenced by randomly assigned code numbers as Lab 101, Lab 102, Lab 103, and Lab 104. These code numbers do not correspond to the above ordered listing of collaborators.

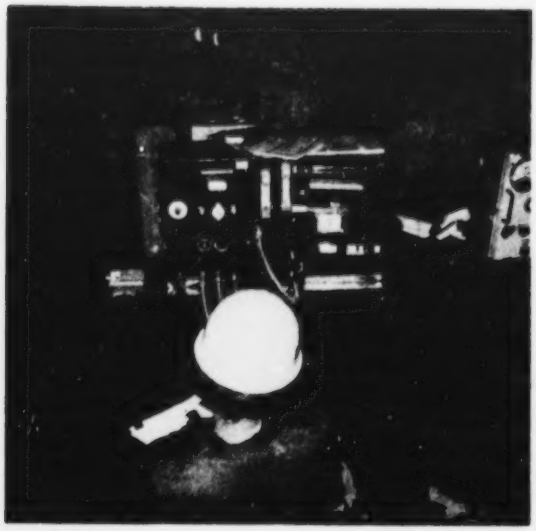


FIGURE 7. CONTROL CONSOLE OPERATION

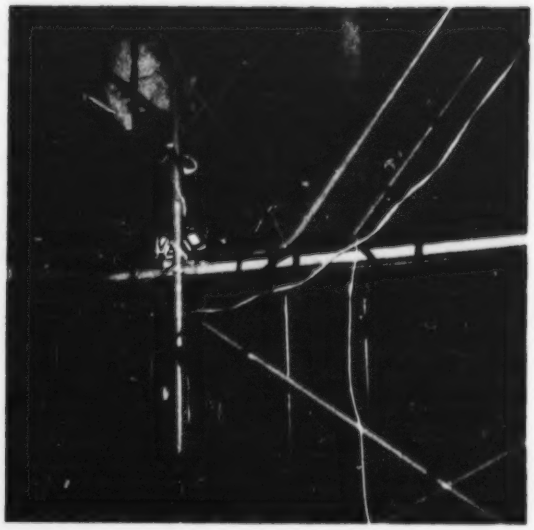


FIGURE 8. IMPINGER TRAIN OPERATION

In Figures 7 and 8, members of the collaborative teams are shown in the operation of an impinger train and a control console during one of the test runs.

C. Philosophy of Collaborative Testing

The concept of collaborative testing followed in the tests discussed in this report involves conducting the test in such a manner as to simulate "real world" testing as closely as possible. "Real world" testing implies that the results obtained during the test by each collaborator would be the same results obtainable if he were sampling alone, without outside supervision and without any additional information from outside sources, i.e., test supervisor or other collaborators.

The function of the test supervisor in such a testing scheme is primarily to see that the method is adhered to as written and that no individual innovations are incorporated into the method by any collaborator. During the test program, the test supervisor observed the collaborators during sampling and sample recovery. If random experimental errors were observed, such as mismeasurement of volume of impinger solution, improper rinsing of probe, etc., no interference was made by the test supervisor. Since such random errors will occur in the everyday use of this method in the field, unduly restrictive supervision of the collaborative test would bias the method with respect to the field test results which will be obtained when the method is put into general usage. However, if gross deviations were observed of such magnitude as to make it clear that the collaborator was not following the method as written, the deviations would be pointed out to the collaborator and corrected by the test supervisor.

While most of the instructions in the *Federal Register*[1] are quite explicit, some areas are subject to interpretation. Where this was the case, the individual collaborators were allowed to exercise their professional judgement as to the interpretation of the instructions.

The overall basis for this so-called "real-world" concept of collaborative testing is to evaluate the subject method in such a manner as to reflect the reliability and precision of the method that would be expected in performance testing in the field.

III. STATISTICAL DESIGN AND ANALYSIS

A. Statistical Terminology

To facilitate the understanding of this report and the utilization of its findings, this section explains the statistical terms used in this report. The procedures for obtaining estimates of the pertinent values are developed and justified in the subsequent sections.

We say that an *estimator*, $\hat{\theta}$, *is unbiased for a parameter* θ if the expected value of $\hat{\theta}$ is θ, or expressed in notational form, $E(\hat{\theta}) = \theta$. From a population of method determinations made at the same true concentration level, μ, let $x_1 \ldots ., x_n$ be a sample of n replicates. Then we define:

(1) $\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$ as the *sample mean*, an unbiased estimate of the ***true determination mean***, δ, the center of the distribution of the determinations. For an accurate method, δ is equal to μ, the true concentration.

(2) $s^2 = \frac{1}{n-1}\sum_{i=1}^{n} (x_i - \bar{x})^2$ as the *sample variance*, an unbiased estimate of the *true variance*, σ^2. This term gives a measure of the dispersion in the distribution of the determinations around δ.

(3) $s = \sqrt{s^2}$ as the sample standard deviation, an alternative measure of dispersion, which estimates σ, *the true standard deviation.*

The sample standard deviation, s, however, is not unbiased for σ,[6] so a *correction factor* needs to be applied. The correction factor for a sample of size n is α_n, and the product of α_n and s is unbiased for σ. That is, $E(\alpha_n s) = \sigma$. As n increases, the value of α_n decreases, going for example from $\alpha_3 = 1.1284$, $\alpha_4 = 1.0854$ to $\alpha_{10} = 1.0281$. The formula for α_n is given in Appendix B.5.

We define

$$\beta = \frac{\sigma}{\delta}$$

as the *true coefficient of variation* for a given distribution. To estimate this parameter, we use a *sample coefficient of variation*, $\hat{\beta}$, defined by

$$\hat{\beta} = \frac{\alpha_n s}{\bar{x}}$$

where $\hat{\beta}$ is the ratio of the unbiased estimates of σ and δ, respectively. The coefficient of variation measures the percentage scatter in the observations about the mean, and thus is a readily understandable way to express the precision of the observations.

The experimental plan for this test called for 16 *runs*. On each run, the collaborative teams were expected to collect simultaneous samples from the stack in accordance with Method 5. Since the actual particulate emission concentration in the stack fluctuates, one can in general expect different true concentrations for each run. To permit a complete statistical analysis, the individual runs are grouped into *blocks*, where each block has approximately the same true emission concentration level.

We can apply the statistical terms of the preceding paragraphs both to the collaborators' values during a given run and to each collaborator's values in a given block. In this report, statistical results from the first situation are referred to as *run results.* Those from the second situation are referred to as *collaborator-block results.* For example, a run mean is the average of each collaborator's concentration level for the run as obtained by Method 5. A collaborator-block coefficient of variation is the ratio of the unbiased standard deviation to the sample mean for all the collaborator's runs grouped in the block.

The variability associated with a Method 5 concentration determination is estimated in terms of the *within-laboratory* and the *between-laboratory precision components.* In addition, a *laboratory bias component* can be estimated. The following definitions of these terms are given with respect to a *true stack concentration,* μ.

- *Within-laboratory*–The within-laboratory standard deviation, σ, measures the *dispersion in replicate single determinations* made using Method 5 by one laboratory team (same field operators, laboratory analyst, and equipment) sampling the same true concentration, μ. The value of σ is estimated from within each collaborator-block combination.

- *Between-laboratory*–The between-laboratory standard deviation, σ_b, measures the *total variability in a concentration determination* due to simultaneous Method 5 determinations by different laboratories sampling the same true stack concentration, μ. The between laboratory variance, σ_b^2, may be expressed as

$$\sigma_b^2 = \sigma_L^2 + \sigma^2$$

  and consists of a within-laboratory variance plus a *laboratory bias variance,* σ_L^2. The between-laboratory standard deviation is estimated using the run results.

- *Laboratory bias*–The laboratory bias standard deviation, $\sigma_L = \sqrt{\sigma_b^2 - \sigma^2}$, is that portion of the total variability that can be ascribed to differences in the field operators, analysts and instrumentation, and due to different manners of performance of procedural details left unspecified in the method. This term measures that part of the total variability in a determination which results from the use of the method by different laboratories, as well as from modifications in usage by a single laboratory over a period of time. The laboratory bias standard deviation is estimated from the within- and between-laboratory estimates previously obtained.

B. Collaborative Test Design

The sampling was done through four ports, two on the east side (EU and EL) and two on the west side (WU and WL). The experiment was designed so that on each day, each collaborator took one sample from the east side ports, and one from the west. At the middle of each run, the collaborators using the upper ports shifted to the lower ones, and those on the lower ports began to use the upper ones. In this manner, any potential port effect was intended to be nullified.

After receiving and making preliminary calculation checks on the data, an attempt was made to group the samples into blocks. Considerations in setting up blocks included time–whether each week constituted a block, load–whether megawatt hour load was a basis for a block, and coal burned–whether the particulate concentration was a function of the amount of coal burned. There is no accurate procedure for the determination of true particulate concentrations, and thus it was impossible to establish blocks based on true or theoretical concentration levels.

The plant provided its daily logs of the hourly operating characteristics of the plant, and the pertinent information was extracted from these logs. It was assumed that the amount of particulate matter which was emitted should depend upon how much fuel was burned. Thus, the average amount of coal burned during the course of each run was determined, and this was selected as the blocking criterion. These amounts are listed in Table 2.

TABLE 2. HOURLY AVERAGE COAL BURNED

Day	Run	Coal Burned ton	Block
8-14	1	351.0	1
	2	247.2	2
8-15	3	304.1	1
	4	322.0	1
8-16	5	231.4	3
	6	300.9	1
8-17	7	232.6	3
	8	228.8	4
8-20	9	232.1	3
	10	241.3	2
8-21	11	246.0	2
	12	214.4	4
8-22	13	225.5	4
	14	244.5	2
8-23	15	229.2	4
	16	238.3	3

Natural blocking of the sample runs appeared to be in groups of four, from the highest fuel burn average to the lowest. The result was four blocks each of size four, in a randomized block design, as will be shown in Table 4.

C. Collaborative Test Data

The concentrations obtained by the collaborators are presented in Table 3. The port sequence used to obtain the sample is also shown. Port sequences are referred to as A (EL to EU), B (EU to EL), C (WU to WL), and D (WL to WU). Reported concentrations marked with a dagger are those for which the isokinetic variation was determined to be outside the acceptable range of 90 to 110 percent.

The concentrations used in the analysis of Method 5 were those reported by Labs 102, 103 and 104 only. The observations from Lab 101 are generally lower than those from the other collaborators. Discussions with personnel at the test site revealed that the glass joints of the filter holder were being sealed with a stopcock grease unsuitable for the high temperatures (250°F+) present in the filter oven. Prior to each run, the sample train was leak checked according to the method. This leak check is performed prior to applying heat to the filter oven. Upon heating the oven, there is a strong possibility that the melting of the low temperature grease used led to the development of leaks during the run. Such leakage around the filter holder fitting would introduce ambient air into the sample train as a diluent, which would lower the concentration level in the sample.

TABLE 3. ORIGINAL PARTICULATE COLLABORATIVE TEST DATA
lb/scf × 10^{-7}*

Sample (Run)	Lab			
	101	102	103	104
1	381.6 (A)†	137.3 (B)	58.4(C)	334.4 (D)†
2	51.4 (C)	191.2 (D)	146.2 (B)	151.5 (A)
3	237.0 (D)	176.8 (C)	225.7 (A)	375.1 (B)
4	85.3 (B)	185.3 (A)	154.9 (C)	103.5 (D)
5	139.7 (A)	194.9 (B)	102.2 (D)	102.8 (C)
6	50.8 (D)	173.6 (C)	146.9 (A)	163.8 (B)
7	114.8 (D)	335.7 (C)	313.9 (B)	132.3 (A)
8	63.8 (A)	190.4 (B)	122.0 (D)	125.9 (C)
9	87.9 (A)	405.3 (B)	197.0 (D)	161.8 (C)
10	72.7 (C)	217.5 (D)	130.9 (B)	151.3 (A)
11	96.0 (D)†	188.5 (C)	124.5 (A)	351.2 (B)
12	103.2 (A)	198.5 (B)	161.8 (C)	111.5 (D)
13	315.2 (B)	210.9 (A)	157.4 (D)	119.4 (C)
14	54.8 (C)	205.2 (D)	107.0 (B)	– (A)
15	112.7 (D)	138.8 (C)	112.3 (A)	123.8 (B)
16	56.5 (B)	167.3 (A)	103.8 (C)	99.9 (D)

( ) Port sequence of sample collection in parenthesis.
*EPA policy is to express all measurements in Agency documents in metric units. When implementing this practice will result in undue cost or difficulty in clarity, NERC/RTP is providing conversion factors for the particular non-metric units used in the document. For this report, the factor is:

10^{-7} lb/scf = 1.6018 × 10^{3} μg/m³.

†Isokinetic variation outside acceptable range.

At the conclusion of the test, inspection of the filter holder assembly revealed that the stopcock grease melted and ran inside the filter holder, saturating half of the fritted glass filter support. The effect of this was not immediately determinable, but it is sufficient cause to suspect the validity of data from Lab 101. On the basis of the above arguments, it was decided to perform the data analysis without that lab's values.

Sample 14 from Lab 104 is missing due to a malfunction in the digital temperature indicator that caused them to abort after beginning the run. In this case, as was the case for the values with unacceptable isokinetic variation factors, no attempt was made to replace the values. The analysis was performed only on those values which were actually taken during the sample period. The concentrations upon which the analysis was performed are presented in Table 4.

D. Precision of Method 5

In a particulate matter determination, no measurement of the accuracy of the method can be obtained. There are no on-stream techniques for analysis and no indicators of true concentration

TABLE 4. PARTICULATE COLLABORATIVE TEST DATA ARRANGED BY BLOCK

Method: EPA Method 5–Determination of Particulate Emissions From Stationary Sources
Test Variable: X = Concentration of Particulates, (lb/scf) x 10^3
Transformation: X Linear
Test Site: Allen King Power Plant
Collaborators: Lab 102, Lab 103, Lab 104.

Inter-Laboratory Run Summary

Block	Run	Lab 102		Lab 103		Lab 104		Run Summary		
		Data	Port*	Data	Port	Data	Port	Mean	Std Dev	Coef of Var
1	1	137.3	(B)	58.4	(C)	334.4E†	(D)	97.8	55.8	0.5702
	3	176.8	(C)	225.7	(A)	375.1	(B)	259.2	103.3	0.3986
	4	185.3	(A)	154.9	(C)	103.5	(D)	147.9	41.3	0.2796
	6	173.6	(C)	146.9	(A)	163.8	(B)	161.4	13.5	0.0837
2	2	191.2	(D)	146.2	(B)	151.5	(A)	163.0	24.6	0.1509
	10	217.5	(D)	130.9	(B)	151.3	(A)	166.6	45.3	0.2718
	11	188.5	(C)	124.5	(A)	351.2	(B)	221.4	116.9	0.5279
	14	205.2	(D)	107.0	(B)	0.0M‡	(A)	156.1	69.4	0.4448
3	5	194.9	(B)	102.2	(D)	102.8	(C)	133.3	53.3	0.4002
	7	335.7	(C)	313.9	(B)	132.3	(A)	260.6	111.7	0.4285
	9	405.3	(B)	197.0	(D)	161.8	(C)	254.7	131.6	0.5167
	16	167.3	(A)	103.8	(C)	99.9	(D)	123.7	37.8	0.3060
4	8	190.4	(B)	122.0	(D)	125.9	(C)	146.1	38.4	0.2629
	12	198.5	(B)	161.8	(C)	111.5	(D)	157.3	43.7	0.2777
	13	210.9	(A)	157.4	(D)	119.4	(C)	162.6	46.0	0.2828
	15	138.8	(C)	112.3	(A)	123.8	(B)	125.0	13.3	0.1063

*Port designation is the sequence of ports from which the sample was taken.
†E indicates an erroneous value due to isokinetic variation being out of acceptable range.
‡M indicates no value was reported for that collaborator in that run.

levels. Also, no type of standard sample for laboratory analysis can be prepared, either, which would give an estimate of lab bias and of the analysis component of the total variation. Thus, the only technique available for evaluating Method 5 is that of estimating the precision of the concentration estimates obtained and the degree to which the results may be duplicated by a separate independent laboratory.

In order to determine our variability estimates, we need to determine what factors have a significant effect on the variation in the reported values. As previously stated, the possibility of a port influence on the concentration obtained was considered, and the test was designed to minimize the effect or the possibility of a lab-port interaction. The hypothesis of no port effect is tested in Appendix B.2 and found to be an acceptable one. As a result, the port factor may be eliminated from further analysis without apparent consequence.

In analyzing the data, two common variance stabilizing transformations, the logarithmic and square root, are applied. For the data under each of these transformations, and the data in its original form (linear), Bartlett's test for homogeneity of variances is used to determine the effect of the transformation. A transformation which satisfies the equality of variance hypothesis gives an indication of the nature of the distribution of the data and of any functional dependence between the mean and the variance or standard deviation of the data. The results of these tests are presented in Appendix B.3.

For the interlaboratory run data, the transformation which achieves the highest degree of equality of variance is the logarithmic. As was demonstrated in a previous collaborative study by Hamil and Camann,[2] this is a strong indication of an underlying linear relationship between the population mean and standard deviation, δ and σ, respectively.

As a further indication, a regression equation is fitted to both the run component and the lab-to-lab component in Appendix B.4. Figure B.1 represents a no-intercept model regression line for the sample means and sample standard deviations from the run data. The correlation coefficient for the model is 0.939. Figure B.2 presents a similar analysis for the collaborator-block means and standard deviations. The correlation coefficient for this model is 0.862. Both values indicate a significant linear relationship at the 5 percent level of significance.

The consequence of this is to provide a model for the variance components, σ^2 and σ_b^2. Let σ^2 be defined as the variance associated with the replicates (samples) within a single laboratory and σ_b^2 be the variance associated with the differences of means between laboratories. From the above argument, we have

$$\sigma = c\delta$$

and

$$\sigma_b = c_b\delta$$

where c and c_b are [unknown] constants. This implies that while δ, σ, and σ_b may vary from run to run or site to site, the relationships σ/δ and σ_b/δ remain constant. If we let

$$\frac{\sigma}{\delta} = \beta$$

and

$$\frac{\sigma_b}{\delta} = \beta_b$$

then we have constant coefficients of variation, β and β_b, for the within-lab and between-lab components, respectively, and σ and σ_b may be defined as a percentage of the mean. In Appendix B.5, this relationship is established, and β and β_b are defined.

In Appendix B.6, the manner of obtaining estimates using a linear combination of the beta values is obtained. The values are given weights relative to the number of determinations used to obtain the estimate. In Appendix B.7, the estimates of the precision components are obtained.

The estimated within-lab coefficient of variation is $\hat{\beta} = (0.311)$, which gives an estimated within-laboratory standard deviation of

$$\hat{\sigma} = \hat{\beta}\delta$$

$$= (0.311)\delta.$$

This estimate has 34 degrees of freedom associated with it.

The estimated between-laboratory coefficient of variation, $\hat{\beta}_b$, is (0.367), which gives an estimated between-laboratory standard deviation of

$$\hat{\sigma}_b = (0.367)\delta.$$

This estimate has 2 degrees of freedom associated with it.

Using these, we can estimate the laboratory bias standard deviation. From the formula in section A.,

$$\hat{\sigma}_L = \sqrt{\hat{\sigma}_b^2 - \hat{\sigma}^2}$$

$$= \sqrt{(0.367)^2\,\delta^2 - (0.311)^2\delta^2}$$

$$= \sqrt{(0.038)\,\delta^2}$$

$$= (0.195)\delta.$$

IV. COMMENTS AND RECOMMENDATIONS

Assessments of Method 5 have been made by the collaborative test supervisor and by the collaborators themselves as a result of their observations and experience in conducting the field testing. These assessments have included the following:

(1) In previous field experience as well as in conversations with many other persons using the method, it has become obvious that this method is more elaborate and time-consuming than most stack sampling methods. This results from mechanical design of the equipment plus the necessity to move heavy equipment items to the sampling point, especially if the sampling point is on a high stack. The necessity for mounting the sampling probe and sample box assembly on a rail for traversing across the stack also complicates the mechanical arrangement of equipment. These difficulties are inherent in the method as published, however, and cannot be avoided.

(2) The extensive use of large amounts of glassware and ground glass connecting joints in the sampling train may result in leaks arising during the course of the run, which will influence the test result.

(3) The movement of equipment required in obtaining a test result often leads to breakage of the glassware used in the sample equipment. In addition, mechanical shock placed on the equipment by raising it to platforms high on the stacks, from which sampling often must be done, can affect the calibration of the equipment as well as cause further glassware damage.

(4) The recovery of particulate matter from the probe is a probable cause of high and low reported concentration levels. During the extraction of the probe, the tip may scrape against the inside of the stack, resulting in an additional amount of particulate matter becoming lodged in the probe tip. This matter is then weighed and analyzed as part of the sample. A loss of particulate matter may occur during the probe wash, if care is not taken. It was noted that, from run to run and collaborator to collaborator, there was considerable variation in the relative amount of particulate collected in the probe wash as compared to the filter collection.

(5) The collaborators observed that the particulate matter collected was extremely hygroscopic. Even though such precautions as placing dishes of desiccant($P_2 O_5$) inside the balance were taken, the accuracy of the particulate weight determinations is doubtful. As a result, the variation in concentration levels between labs is doubtlessly affected by the manner in which the filter particulate collection was handled as it was being weighed.

The comments presented above and the conclusions previously drawn provide a firm basis for the following recommendations.

(1) Further testing at power plants is warranted in order to assess the precision of Method 5. The relatively high values for the precision estimates may be representative of the true values. However, with usable data from only three of the collaborators, and with only one site being tested, these results are inconclusive, and additional testing should be arranged.

(2) The collaborators made frequent calculation errors in the collaborative test data and there were differences among labs in the number of significant digits carried. To prevent these from unfairly influencing the result of a performance test for compliance, it is recommended that a standard Method 5 computer program be written to calculate compliance test results from raw field data.

(3) It is recommended that a standard technique for cleaning the filter apparatus be specified in detail in the method. As it stands now, the cleaning technique used varies somewhat from lab to lab, depends greatly on the carefulness of the laboratory team, and is undoubtedly a major source of error.

(4) It is recommended that the technique for cleaning the probe be specified in greater detail in the method. Much of the variation in the method results from the probe cleaning, and details should be included in the

method concerning the handling of the probe during sample recovery and the manner of recovering particulate matter from the probe.

(5) During sampling, many problems arise from the equipment used to obtain the samples. The design and reliability of much of the equipment now available for use with Method 5 do not seem adequate. As previously noted, the amount of glassware used in the equipment leads to unreliability, both in the equipment itself (from the high breakage levels) and in the performance (due to the probability of leaks arising during the course of the run). It is recommended that improvements be made in the equipment design and that efforts be made to eliminate the use of glassware and ground glass joints wherever possible. Improvements in this area should be made at an early date, if at all feasible.

By implementing these recommendations, the variation associated with Method 5 test results, both within- and between-laboratory, should be able to be better separated from analytical and mechanical components.

APPENDIX A

METHOD 5–DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES

Federal Register, Vol. 36, No. 247
December 23, 1971

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2.1.4 Filter Holder—Pyrex[1] glass with heating system capable of maintaining minimum temperature of 225° F.

2.1.5 Impingers / Condenser—Four impingers connected in series with glass ball joint fittings. The first, third, and fourth impingers are of the Greenburg-Smith design, modified by replacing the tip with a ½-inch ID glass tube extending to one-half inch from the bottom of the flask. The second impinger is of the Greenburg-Smith design with the standard tip. A condenser may be used in place of the impingers provided that the moisture content of the stack gas can still be determined.

2.1.6 Metering system—Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 5° F., dry gas meter with 2% accuracy, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume.

2.1.7 Barometer—To measure atmospheric pressure to ±0.1 inches Hg.

2.2 Sample recovery.

2.2.1 Probe brush—At least as long as probe.

2.2.2 Glass wash bottles—Two.

2.2.3 Glass sample storage containers.

2.2.4 Graduated cylinder—250 ml.

2.3 Analysis.

2.3.1 Glass weighing dishes.

2.3.2 Desiccator.

2.3.3 Analytical balance—To measure to ±0.1 mg.

2.3.4 Trip balance—300 g. capacity, to measure to ±0.05 g.

3. *Reagents.*

3.1 Sampling.

3.1.1 Filters—Glass fiber, MSA 1106 BH[1], or equivalent, numbered for identification and preweighed.

3.1.2 Silica gel—Indicating type, 6–16 mesh, dried at 175° C. (350° F.) for 2 hours.

3.1.3 Water.

3.1.4 Crushed ice.

3.2 Sample recovery.

3.2.1 Acetone—Reagent grade.

3.3 Analysis.

3.3.1 Water.

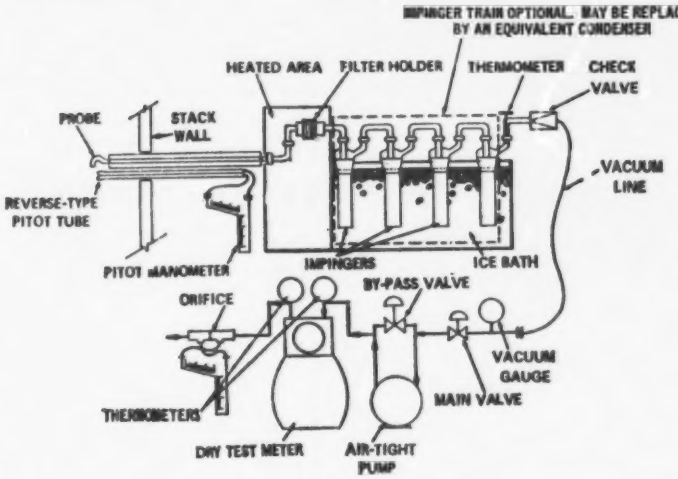

Figure 5-1. Particulate-sampling train.

3.3.2 Desiccant—Drierite,[2] indicating.

4. *Procedure.*

4.1 Sampling

4.1.1 After selecting the sampling site and the minimum number of sampling points, determine the stack pressure, temperature, moisture, and range of velocity head.

4.1.2 Preparation of collection train. Weigh to the nearest gram approximately 200 g. of silica gel. Label a filter of proper diameter, desiccate[2] for at least 24 hours and weigh to the nearest 0.5 mg. in a room where the relative humidity is less than 50%. Place 100 ml. of water in each of the first two impingers, leave the third impinger empty, and place approximately 200 g. of preweighed silica gel in the fourth impinger. Set up the train without the probe as in Figure 5-1. Leak check the sampling train at the sampling site by plugging up the inlet to the filter holder and pulling a 15 in. Hg vacuum. A leakage rate not in excess of 0.02 c.f.m. at a vacuum of 15 in. Hg is acceptable. Attach the probe and adjust the heater to provide a gas temperature of about 250° F. at the probe outlet. Turn on the filter heating system. Place crushed ice around the impingers. Add more ice during the run to keep the temperature of the gases leaving the last impinger as low as possible and preferably at 70° F. or less. Temperatures above 70° F. may result in damage to the dry gas meter from either moisture condensation or excessive heat.

4.1.3 Particulate train operation. For each run, record the data required on the example sheet shown in Figure 5-2. Take readings at each sampling point, at least every 5 minutes, and when significant changes in stack conditions necessitate additional adjustments in flow rate. To begin sampling, position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Sample for at least 5 minutes at each traverse point; sampling time must be the same for each point. Maintain isokinetic sampling throughout the sampling period. Nomographs are available which aid in the rapid adjustment of the sampling rate without other computations. APTD–0576 details the procedure for using these nomographs. Turn off the pump at the conclusion of each run and record the final readings. Remove the probe and nozzle from the stack and handle in accordance with the sample recovery process described in section 4.2.

METHOD 5—DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and applicability.*

1.1 Principle. Particulate matter is withdrawn isokinetically from the source and its weight is determined gravimetrically after removal of uncombined water.

1.2 Applicability. This method is applicable for the determination of particulate emissions from stationary sources only when specified by the test procedures for determining compliance with New Source Performance Standards.

2. *Apparatus.*

2.1 Sampling train. The design specifications of the particulate sampling train used by EPA (Figure 5–1) are described in APTD–0581. Commercial models of this train are available.

2.1.1 Nozzle—Stainless steel (316) with sharp, tapered leading edge.

2.1.2 Probe—Pyrex[1] glass with a heating system capable of maintaining a minimum gas temperature of 250° F. at the exit end during sampling to prevent condensation from occurring. When length limitations (greater than about 8 ft.) are encountered at temperatures less than 600° F., Incoloy 825[1], or equivalent, may be used. Probes for sampling gas streams at temperatures in excess of 600° F. must have been approved by the Administrator.

2.1.3 Pitot tube—Type S, or equivalent, attached to probe to monitor stack gas velocity.

[1] Trade name.

[2] Dry using Drierite[1] at 70° F. ± 10° F.

[1] Trade name.

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PLANT _____
LOCATION _____
OPERATOR _____
DATE _____
RUN NO. _____
SAMPLE BOX NO. _____
METER BOX NO. _____
METER $\Delta H_@$ _____
C FACTOR _____

SCHEMATIC OF STACK CROSS SECTION

AMBIENT TEMPERATURE _____
BAROMETRIC PRESSURE _____
ASSUMED MOISTURE, % _____
HEATER BOX SETTING _____
PROBE LENGTH, in. _____
NOZZLE DIAMETER, in. _____
PROBE HEATER SETTING _____

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	STATIC PRESSURE (P_g), in. Hg	STACK TEMPERATURE (T_s), °F	VELOCITY HEAD (Δp),	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER (ΔH), in. H_2O	GAS SAMPLE VOLUME (Vm), ft^3	GAS SAMPLE TEMPERATURE AT DRY GAS METER		SAMPLE BOX TEMPERATURE, °F	TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °F
							INLET ($T_{m_{in}}$), °F	OUTLET ($T_{m_{out}}$), °F		
TOTAL							Avg.	Avg.		
AVERAGE							Avg.			

Figure 5-2. Particulate field data.

4.2 Sample recovery. Exercise care in moving the collection train from the test site to the sample recovery area to minimize the loss of collected sample or the gain of extraneous particulate matter. Set aside a portion of the acetone used in the sample recovery as a blank for analysis. Measure the volume of water from the first three impingers, then discard. Place the samples in containers as follows:

Container No. 1. Remove the filter from its holder, place in this container, and seal.

Container No. 2. Place loose particulate matter and acetone washings from all sample-exposed surfaces prior to the filter in this container and seal. Use a razor blade, brush, or rubber policeman to lose adhering particles.

Container No. 3. Transfer the silica gel from the fourth impinger to the original container and seal. Use a rubber policeman as an aid in removing silica gel from the impinger.

4.3 Analysis. Record the data required on the example sheet shown in Figure 5-3. Handle each sample container as follows:

Container No. 1. Transfer the filter and any loose particulate matter from the sample container to a tared glass weighing dish, desiccate, and dry to a constant weight. Report results to the nearest 0.5 mg.

Container No. 2. Transfer the acetone washings to a tared beaker and evaporate to dryness at ambient temperature and pressure. Desiccate and dry to a constant weight. Report results to the nearest 0.5 mg.

Container No. 3. Weigh the spent silica gel and report to the nearest gram.

5. *Calibration.*

Use methods and equipment which have been approved by the Administrator to calibrate the orifice meter, pitot tube, dry gas meter, and probe heater. Recalibrate after each test series.

6. *Calculations.*

6.1 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 5-2).

6.2 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions (70° F., 29.92 inches Hg) by using Equation 5-1.

$$V_{m_{std}} = V_m \left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}}\right) = \left(17.71 \frac{°R}{\text{in. Hg}}\right) V_m \left(\frac{P_{bar} + \frac{\Delta H}{13.6}}{T_m}\right)$$

equation 5-1

where:

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

V_m = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_{std} = Absolute temperature at standard conditions, 530° R.

T_m = Average dry gas meter temperature, °R.

P_{bar} = Barometric pressure at the orifice meter, inches Hg.

ΔH = Average pressure drop across the orifice meter, inches H_2O.

13.6 = Specific gravity of mercury.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

6.3 Volume of water vapor.

$$V_{w_{std}} = V_{l_c}\left(\frac{\rho_{H_2O}}{M_{H_2O}}\right)\left(\frac{RT_{std}}{P_{std}}\right) = \left(0.0474 \frac{\text{cu. ft.}}{\text{ml.}}\right) V_{l_c}$$

equation 5-2

where:

$V_{w_{std}}$ = Volume of water vapor in the gas sample (standard conditions), cu. ft.

V_{l_c} = Total volume of liquid collected in impingers and silica gel (see Figure 5-3), ml.

ρ_{H_2O} = Density of water, 1 g./ml.

M_{H_2O} = Molecular weight of water, 18 lb./lb.-mole.

R = Ideal gas constant, 21.83 inches Hg—cu. ft./lb.-mole-°R.

T_{std} = Absolute temperature at standard conditions, 530° R.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

6.4 Moisture content.

$$B_{ws} = \frac{V_{w_{std}}}{V_{m_{std}} + V_{w_{std}}}$$

equation 5-3

where:

B_{ws} = Proportion by volume of water vapor in the gas stream, dimensionless.

$V_{w_{std}}$ = Volume of water in the gas sample (standard conditions), cu. ft.

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

6.5 Total particulate weight. Determine the total particulate catch from the sum of the weights on the analysis data sheet (Figure 5-3).

6.6 Concentration.

6.6.1 Concentration in gr./s.c.f.

$$c'_s = \left(0.0154 \frac{\text{gr.}}{\text{mg.}}\right)\left(\frac{M_n}{V_{m_{std}}}\right)$$

equation 5-4

where:

c'_s = Concentration of particulate matter in stack gas, gr./s.c.f., dry basis.

M_n = Total amount of particulate matter collected, mg.

$V_{m_{std}}$ = Volume of gas sample through dry gas meter (standard conditions), cu. ft.

APPENDIX B

STATISTICAL METHODS

STATISTICAL METHODS

This appendix consists of various sections which contain detailed statistical procedures carried out in the analysis of the particulate matter collaborative study data. Reference to these sections has been made at various junctures in the Statistical Design and Analysis part of the body of this report. Each Appendix B section is an independent ad hoc statistical analysis pertinent to a particular problem addressed in the body of the report.

B.1 Preliminary Analysis of the Original Collaborative Test Data

Preliminary checks were made on the originally reported data in order to eliminate calculation errors and to ensure that all concentrations were obtained using the specified formulas and correction factors. In this manner, results presented are representative of actual differences in the concentration levels found, rather than due to improper or inaccurate use of the equations. Thus, we can discern more clearly the variability that is associated with Method 5 itself.

The concentrations from the three collaborators, Labs 102, 103, and 104, were analyzed with two missing observations. In Run 1, Lab 104 was only 77 percent of isokinetic, and the result was considered invalid. On Run 14, Lab 104 was forced to abort as a result of equipment malfunction, and no value was reported. The analysis was performed on the remainder of the observations, with no attempt to replace these values.

In each lab, there are values which appear, at first glance, to be outliers. These are of a magnitude of approximately twice that of the rest of the samples for that lab. However, these occurred with such regularity (2 to 3/lab) that it was decided not to make any adjustment for them in the analysis. Indeed, they appear to be representative of the type of error that occurs when Method 5 is used on a power plant.

B.2 Significance of the Port Effect

The sampling at the Allen S. King Power Plant was done through four sample ports, two on either side of the duct. The ports were designated East Upper, East Lower, West Upper, and West Lower (EU, EL, WU, WL). On each run, a sampling team began on one side at either the upper or the lower port, shifting at the halfway point of the run to the other port on the same side. The result is four port combination patterns: EL to EU, EU to EL, WU to WL, WL to WU, assigned the designations A, B, C and D respectively.

The test for port effect was made using the four sequences as different ports, rather than merely East vs West. It is felt that this provides a more complete evaluation of the possible differences. The analysis is done using Youden's[4] rank test.

Each sequence is assigned a rank within each run. The ranks are then summed for each sequence and the results compared against confidence limits tabled by Youden. The test is presented in Table B.1.

The null hypothesis to be tested is that there is no port (port sequence) effect. This hypothesis may be rejected, at the 0.05 level of significance, only if the high port sum or the low port sum falls outside the limits of the confidence interval. Since the highest sum, 44 (WL to WU), is less than the upper limit of 52, and the smallest sum, 33 (EU to EL) is greater than the lower limit of 28, the hypothesis may not be rejected. Thus, we can assume no differences due to ports, and further analysis is done under that assumption.

B.3 Transformations

As a means of obtaining information about the nature of the distribution of the concentrations, the values were examined to determine what kind of transformation best gives an equality of variance for the sample data.

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TABLE B.1. SIGNIFICANCE OF PORT EFFECT

Youden's Rank Test

Run	Port*			
	A	B	C	D
1	1	3	4	2
2	2	3	4	1
3	3	1	4	2
4	1	4	2	3
5	2	1	3	4
6	3	2	1	4
7	3	2	1	4
8	4	1	2	3
9	4	1	3	2
10	2	3	4	1
11	3	1	2	4
12	4	1	2	3
13	2	1	4	3
14	1	3	4	2
15	4	2	1	3
16	1	4	2	3
Rank Sums	40	33	43	44

H_O: No Port Effect

$CI_{0.95}$ (28, 52)

Conclusion: Accept H_O, No Port Effect

*Port Sequences:
A(EL to EU),
B(EU to EL),
C(WU to WL),
D(WL to WU).

TABLE B.2. DATA TRANSFORMATION TO ACHIEVE RUN EQUALITY OF VARIANCE

Transformation	Test Statistic	Degrees of Freedom	Significance
Linear	19.071	15	0.20
Logarithmic	10.902	15	0.75
Square Root	13.753	15	0.55

For each transformation used, Bartlett's test for homogeneity of variance was used to ascertain the degree of equality obtained.

The data were examined in their original form (linear) and passed through two transformations, the logarithmic and the square root. The results are presented in Table B.2 for the run component data. The significance levels are taken from a table of χ^2 with 15 degrees of freedom.

The logarithmic transformation clearly attains the best results, implying that the run data follow the lognormal distribution. In addition, this is an indication, as presented in Hamil and Camann[2], that there is an underlying linear relationship between the mean and the standard deviation of the distribution of the run data.

B.4 Empirical Relationship of the Mean and Standard Deviation in the Collaborative Test Data

In order to properly analyze the data from the collaborative test, it is necessary to investigate the relationship between the mean and the standard deviation for both the interlaboratory and intralaboratory components. We wish to determine to what extent the variability in the concentrations is related to the actual concentration level. Therefore, let

x_{ijk} be the concentration reported by lab i in block j of run k.

$\bar{x}_{.jk}$ be the mean for run k in block j across labs,

$s_{jk} = \sqrt{\frac{1}{2}\sum_{i=1}^{3}(x_{ijk} - \bar{x}_{.jk})^2}$, be the run standard deviation, assuming 3 collaborators.

Table B.3 gives the values of the sample means and standard deviations obtained from the St. Paul test. Asterisks denote those values taken over only two responses due to a missing or erroneous data point.

By visual inspection, it appears that there is a linear trend between $\bar{x}_{.jk}$ and s_{jk}; that is, as $\bar{x}_{.jk}$ increases, so does s_{jk}. A least squares regression line is calculated for these points and presented in Figure B-1. A no-intercept model is used since a mean of zero could only logically occur when each reported concentration was identically equal to zero, thus resulting in a zero standard deviation.

A correlation coefficient between $\bar{x}_{.jk}$ and s_{jk} is calculated to be 0.939 for the no-intercept model. This value is significant at a level greater than 10 percent. The coefficient of determination is 0.881, indicating 88.1 percent of the variation in the magnitude of the standard deviation is attributed to the variation in the magnitude of the sample mean.

TABLE B.3. INTERLABORATORY RUN SUMMARY

Block	Run	Mean lb/scf × 10^7	Std Dev lb/scf × 10^7
1	*1	97.85	55.79
	3	259.20	103.31
	4	147.90	41.35
	6	161.43	13.51
2	2	162.97	24.59
	10	166.57	45.27
	11	221.40	116.88
	*14	156.10	69.44
3	5	133.30	53.35
	7	260.63	111.67
	9	254.70	131.61
	16	123.67	37.84
4	8	146.10	38.41
	12	157.27	43.68
	13	162.57	45.97
	15	124.97	13.29

*Runs with only 2 determinations.

Thus, we have empirical evidence that the linear relationship indicated by the transformation data in Appendix B.3 is present.

We can perform a similar analysis for the intralaboratory collaborator-block data. Let us denote

$\bar{x}_{ij\cdot}$ as the mean for collaborator i, block j

$s_{ij} = \sqrt{\frac{1}{3}\sum_{i=1}^{4}(x_{ijk} - \bar{x}_{ij\cdot})^2}$ as the collaborator-block standard deviation, assuming four runs per block.

The values obtained for $\bar{x}_{ij\cdot}$ and s_{ij} are presented in Table B.4. Asterisks denote those values based on only three runs due to missing values. A no-intercept regression line is fitted to

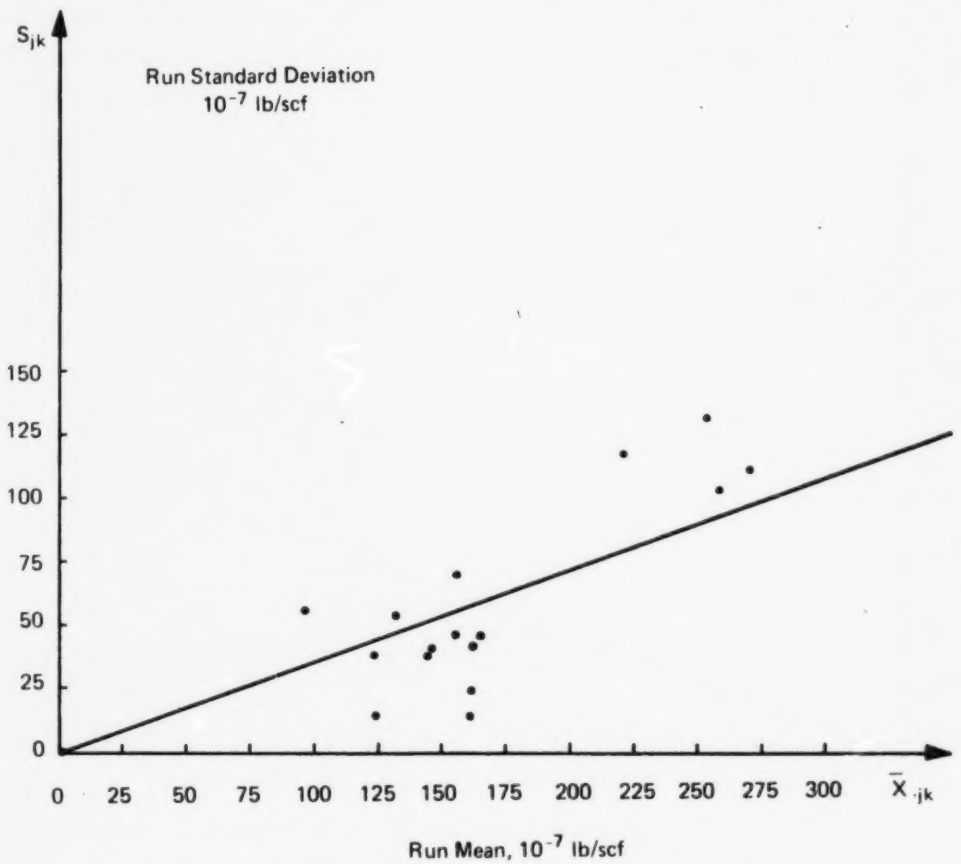

FIGURE B.1. INTERLABORATORY RUN PLOT

TABLE B.4. INTRALABORATORY COLLABORATOR-BLOCK SUMMARY

Block	Collaborator	Mean, lb/scf × 10^7	Std Dev lb/scf × 10^7
1	Lab 102	168.25	21.22
	Lab 103	146.47	68.57
	Lab 104*	214.13	142.62
2	Lab 102	200.60	13.44
	Lab 103	127.15	16.23
	Lab 104*	218.00	115.35
3	Lab 102	275.80	113.54
	Lab 103	179.22	100.13
	Lab 104	124.20	29.03
4	Lab 102	184.65	31.71
	Lab 103	138.37	24.89
	Lab 104	120.16	6.37

*Blocks with only three observations.

these points and represented in Figure B.2. As before, the linear tendency of the s_{ij}'s relative to the $\bar{x}_{ij}$.'s is apparent.

The value of the correlation coefficient is 0.862, which again has a significance level greater than 10 percent. The coefficient of determination is 0.742.

B.5 Underlying Relationship Between the Mean and Standard Deviation

In Appendix B.4, the empirical relationship between the mean and standard deviation for the between-laboratory components is established. This implies that

$$s_{ij} = b\bar{x}_{ij}.$$

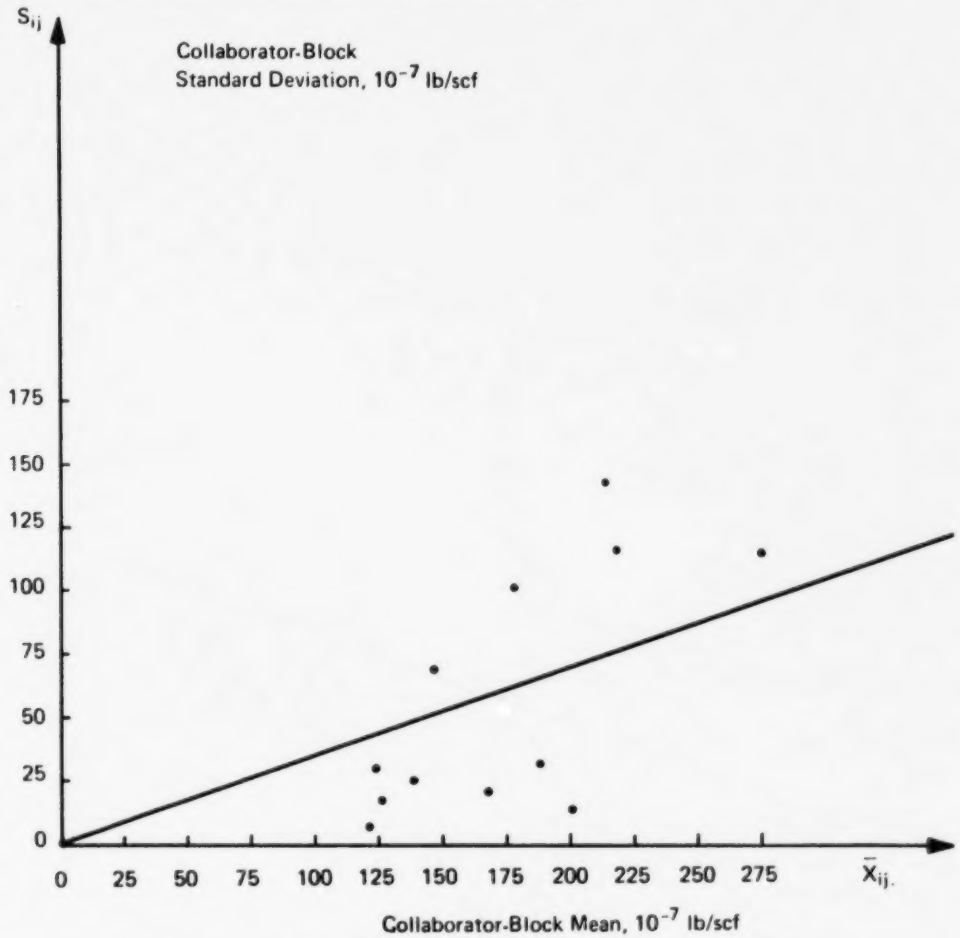

FIGURE B.2. INTRALABORATORY COLLABORATOR-BLOCK PLOT

TABLE B.5. BIAS CORRECTION FACTORS FOR SAMPLE STANDARD DEVIATIONS

n	α_n
2	1.2533
3	1.1284
4	1.0854

where b is the sample coefficient of variation. The collaborator block standard deviation, s_{ij}, represents an estimate of the within-lab standard deviation, σ. However, it has been shown[5] that the sample standard deviation is a biased estimate and that a correction factor must be applied to remove the bias. The correction factor is given by

$$\alpha_n = \sqrt{\frac{2}{3}} \frac{\Gamma\left(\frac{n}{2}\right)}{\Gamma\left(\frac{n-1}{2}\right)}$$

where n is the size of the sample, and Γ represents the standard gamma function. Values of α_n are presented in Table B.5.

Thus, $E(\alpha_n s_{ij}) = \sigma$ and

$$\begin{aligned} \sigma &= E(\alpha_n s_{ij}) \\ &= \alpha_n E(s_{ij}) \\ &= \alpha_n E(b\bar{x}_{ij}.) \\ &= \alpha_n b E(\bar{x}_{ij}.) \\ &= \alpha_n b \delta \end{aligned}$$

If we let $\beta = \alpha_n b$, we have

$$\sigma = \beta\delta$$

where σ and δ are the true mean and standard deviation for the distribution of the collaborator-block data.

In Appendices B.3 and B.4, the linear relationship between the run mean and standard deviation is established, that is

$$s_{jk} = b'\bar{x}_{.jk}$$

where b' represents the sample coefficient of variation for the run data. The expected value of s_{jk}^2 is $\sigma^2 + \sigma_L^2$, a within-laboratory component plus a laboratory bias component. As before, s_{jk} is a biased estimator for $\sqrt{\sigma^2 + \sigma_L^2}$, and the bias may be corrected in the same manner. Thus we have

$$\begin{aligned} \sqrt{\sigma^2 + \sigma_L^2} &= E(\alpha_n s_{jk}) \\ &= \alpha_n E(s_{jk}) \\ &= \alpha_n E(b'\bar{x}_{.jk}) \\ &= \alpha_n b' E(\bar{x}_{.jk}) \\ &= \alpha_n b'\delta \end{aligned}$$

and defining $\beta_b = \alpha_n b'$, we have

$$\sqrt{\sigma_L^2 + \sigma^2} = \beta_b \delta$$

where σ_L^2 represents the true laboratory bias variation. From this relationship, it can be shown[2] that

$$\sigma_L = [\sqrt{\beta_b^2 - \beta^2}]\,\delta$$

or

$$\sigma_L = \beta_L \delta$$

where

$$\beta_L = \sqrt{\beta_b^2 - \beta^2}$$

Thus, it is established that for both the within-laboratory component and the laboratory bias component, there is a linear relationship between the standard deviations, σ and σ_L, and the mean δ.

B.6 Weighted Coefficient of Variation Estimates

The technique used for obtaining estimates of the coefficients of variation of interest is to use a linear combination of the individual beta values obtained. The linear combination used will be of the form

$$\frac{1}{k}\sum_{j=1}^{k} w_j \hat{\beta}_j$$

where $\hat{\beta}_j$ is the jth coefficient of variation estimate, k is the total number of estimates, and w_j is a weight applied to the jth estimate.

As previously discussed, the individual estimate of β is obtained as

$$\hat{\beta} = \frac{\alpha_n s}{\bar{x}}$$

for a sample of size n. This estimator is shown in B.5 to be unbiased for the true coefficient of variation. However, since we are dealing with small samples to obtain our individual estimates, weighting is more desirable in that it provides for more contribution from those values derived from larger samples. There is more variability in the beta values obtained from the smaller samples, as can be seen by inspecting the variance of the estimator. We have that

$$\mathrm{Var}(\hat{\beta}) = \mathrm{Var}\left(\frac{\alpha_n s}{\bar{x}}\right)$$

$$= \alpha_n^2 \ \mathrm{Var}\left(\frac{s}{\bar{x}}\right)$$

$$= \alpha_n^2 \left[\frac{\beta^2}{2n}(1 + 2\beta^2)\right]$$

for normally distributed samples,[3] and true coefficient of variation, β. Rewriting this expression, we have

$$\mathrm{Var}(\hat{\beta}) = \frac{\alpha_n^2}{n}\left[\frac{\beta^2}{2}(1 + 2\beta^2)\right]$$

and all terms are constant except for α_n^2 and n. Thus, the magnitude of the variance changes with respect to the factor α_n^2/n. Now, since α_n decreases as n increases, the factor α_n^2/n must decrease as n increases, and the variance is reduced.

The weights, w_j, are determined according to the technique used in weighted least squares analysis[6], which gives a minimum variance estimate of the parameter. The individual weight, w_i, is computed as the inverse of the variance of the estimate, $\hat{\beta}_i$, and then standardized. Weights are said to be standardized when

$$\frac{1}{k}\sum_{j=1}^{k} w_j = 1$$

To standardize, the weights are divided by the average of the inverse variances for all the estimates. Thus, we can write

$$w_i = \frac{u_i}{\bar{u}}$$

where

$$u_i = \frac{1}{\mathrm{Var}(\hat{\beta}_i)}$$

and

$$\bar{u} = \frac{1}{k}\sum_{j=1}^{k}\frac{1}{\mathrm{Var}(\hat{\beta}_j)}$$

Now, from the above expressions, we can determine u_i, $\bar{u}$ and w_i for the beta estimates. For any estimate, β_i,

$$u_i = \frac{1}{\mathrm{Var}(\beta_i)}$$

$$= \frac{n_i}{\alpha_{n_i}^2}\left[\frac{2}{\beta^2(1 + 2\beta^2)}\right]$$

for sample size n_i, and

$$\bar{u} = \frac{1}{k}\sum_{j=1}^{k}\frac{1}{\mathrm{Var}(\beta_j)}$$

$$= \frac{1}{k}\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}\left[\frac{2}{\beta^2(1 + 2\beta^2)}\right]$$

$$= \frac{1}{k}\left[\frac{2}{\beta^2(1 + 2\beta^2)}\right]\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}.$$

Thus, the ith weight, w_i, is

$$w_i = \frac{u_i}{\bar{u}}$$

$$= \frac{\dfrac{n_i}{\alpha_{n_i}^2}\left[\dfrac{2}{\beta^2(1+2\beta^2)}\right]}{\dfrac{1}{k}\left[\dfrac{2}{\beta^2(1+2\beta^2)}\right]\sum\dfrac{n_j}{\alpha_{n_j}^2}}$$

$$= \frac{\dfrac{n_i}{\alpha_{n_i}^2}}{\dfrac{1}{k}\displaystyle\sum_{i=1}^{k}\frac{n_j}{\alpha_{n_j}^2}}$$

$$= \frac{\dfrac{kn_i}{\alpha_{n_i}^2}}{\displaystyle\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}}$$

The estimated coefficient of variation is

$$\hat{\beta} = \frac{1}{k}\sum_{j=1}^{k} w_j\hat{\beta}_i$$

$$= \frac{1}{k}\sum_{i=1}^{k}\frac{kn_i\alpha_{n_i}^2}{\displaystyle\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}}\,\hat{\beta}_i$$

$$= \left[\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}\right]^{-1}\sum_{i=1}^{k}\frac{n_i}{\alpha_{n_i}^2}\cdot\frac{\alpha_{n_i}s}{\bar{x}}$$

$$= \left[\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}\right]^{-1}\sum_{i=1}^{k}\frac{n_i s}{\alpha_{n_i}\bar{x}}.$$

B.7 Estimating Standard Deviation Components

In Appendix B.3 and B.4, the relationships for the between-laboratory and within-laboratory standard deviations, σ_b and σ, are established as

$$\sigma_b = \beta_b.\delta$$

and

$$\sigma = \beta\delta$$

where β_b and β represent the true coefficients of variation, and δ is the true mean determination. In Appendix B.5 it is shown that for the laboratory bias standard deviation, σ_L, the above expressions imply

$$\sigma_L = \beta_L \delta$$

$$= (\sqrt{\beta_b^2 - \beta^2})\,\delta.$$

In Appendix B.6, the technique for obtaining an unbiased estimate of a coefficient of variation as a linear combination of the individual values is discussed. The estimator is of the form

$$\hat{\beta} = \frac{1}{k} \sum_{i=1}^{k} w_i \hat{\beta}_i$$

where $\hat{\beta}$ is the estimated beta from the ith sample and w_i is a weight applied. For the between-laboratory coefficient of variation, this becomes

$$\hat{\beta}_b = \frac{1}{16} \sum_{i=1}^{16} w_i \hat{\beta}_i$$

TABLE B.6 RUN BETA VALUES AND WEIGHTS

Run	Beta Hat	Weight
1	0.7146	0.573
2	0.1703	1.061
3	0.4497	1.061
4	0.3155	1.061
5	0.4516	1.061
6	0.0944	1.061
7	0.4835	1.061
8	0.2967	1.061
9	0.5831	1.061
10	0.3067	1.061
11	0.5957	1.061
12	0.3134	1.061
13	0.3191	1.061
14	0.5575	0.573
15	0.1200	1.061
16	0.3453	1.061

TABLE B.7 COLLABORATOR-BLOCK BETA VALUES AND WEIGHTS

Block	Collaborator	Beta Hat	Weight
1	Lab 102	0.1369	1.054
	Lab 103	0.5081	1.054
	Lab 104	0.7516	0.731
2	Lab 102	0.0727	1.054
	Lab 103	0.1385	1.054
	Lab 104	0.5971	0.731
3	Lab 102	0.4468	1.054
	Lab 103	0.6064	1.054
	Lab 104	0.2537	1.054
4	Lab 102	0.1864	1.054
	Lab 103	0.1952	1.054
	Lab 104	0.0576	1.054

The individual beta values and their weights are shown in Table B.6. Substituting these into the formula we have

$$\hat{\beta}_b = (0.367)$$

and as a result

$$\hat{\sigma}_b = \hat{\beta}_b \delta$$

$$= (0.367)\delta$$

For $p = 3$ laboratories, there are $3 - 1 = 2$ degrees of freedom associated with this estimate.

Similarly, for the within-laboratory coefficient of variation, we have

$$\hat{\beta} = \frac{1}{12} \sum_{j=1}^{12} w_j \hat{\beta}_j$$

where $\hat{\beta}_j$ is an estimated beta value from a collaborator-block combination, and w_j is the corresponding weight. The individual values and their weights are shown in Table B.7. Substituting into the above formula, we obtain

$$\hat{\beta} = (0.311)$$

which implies that

$$\hat{\sigma} = \hat{\beta}\delta$$

$$= (0.311)\delta.$$

For the 12 collaborator-blocks, this results in $46 - 12 = 34$ degrees of freedom for this estimate.

Using these values in the equation for the laboratory bias coefficient of variation, we estimate β_L as

$$\hat{\beta}_L = \sqrt{(0.367)^2 - (0.311)^2}$$

$$= \sqrt{0.038}$$

$$= 0.195.$$

Thus, the estimated laboratory bias standard deviation is

$$\hat{\sigma}_L = \hat{\beta}_L \delta$$

$$= (0.195)\delta.$$

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